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# **EUROPEAN PATENT APPLICATION**

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㉔ Insecticidal compositions, and preparation and use thereof.

㉕ Insecticidal compositions and the preparation and use thereof are disclosed. Substantially solvent-free microcapsules comprising a core of an insecticide selected from the group consisting of methomyl, oxamyl, and mixtures of methomyl with oxamyl or other known insecticides within an encapsulating wall of a cross-linked polyurea are disclosed. The microcapsules may be made by dissolving the insecticide(s) in methylene chloride containing a polyisocyanate, emulsifying the solution and adding a diamine or polyamine to form a cross-linked polyurea encapsulating shell around droplets of the emulsifying solution, followed by removal of methylene chloride. Compositions containing the microcapsules are also disclosed.

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"Insecticidal Compositions, and Preparation  
and use thereof"

This invention relates to insecticidal compositions and the preparation and use thereof. More particularly  
5 it relates to compositions containing methomyl.

Methomyl and oxamyl are known important insecticides. They are known chemically as:  
S-methyl N-[(methylcarbamoyl)oxythioacetamide] (methomyl)  
and S-methyl N,N'-dimethyl-N-[(methylcarbamoyl)oxy]-1-  
10 thiooxamimidate (oxamyl).

These insecticides have certain disadvantages, however. Methomyl controls boll weevil but is phytotoxic to cotton under some conditions. Methomyl also has short residual activity, i.e., it breaks down  
15 to nontoxic compounds in about three days; this is an advantage from the standpoint of environmental safety, but a disadvantage in that multiple applications are required for effective insect control. In addition, methomyl and oxamyl are toxic to mammals,  
20 and they require careful handling and use.

A technique for reducing the mammalian toxicity and phytotoxicity and increasing the residual activity of methyl and ethyl parathion insecticides is taught in U.S. Patent Specification No.  
25 3,959,464. The technique involves encapsulating the insecticide within a wall of cross-linked polyamide-polyurea by emulsifying the liquid insecticide and polyfunctional monomer (acid chloride or isocyanate) in water, adding complementary monomer and permitting the monomers to react to form  
30 the cross-linked polyamide polyurea. The resulting microcapsules range in average particle size from about 30 to 130 microns and contain a weight ratio of pesticide to polymer in the range of 2:1 to 10:1. The technique of U.S. Patent Specification No. 3,959,464 is  
35 not useful for encapsulating methomyl and oxamyl because these materials, unlike the parathions, are solids

at room temperature. Moreover, both methomyl and oxamyl are water soluble solids, which does not allow for their emulsification in an aqueous phase.

In Example XII of British Patent Specification No. 1,371,179, a process is disclosed involving encapsulation of a solid insecticide by dissolving it and a mixture of isocyanates in naphtha, addition of this solution to water and agitation to form an emulsion. A portion of the isocyanate hydrolyzes to amine which then reacts with isocyanate to form a polyurea encapsulating shell. A disadvantage of this procedure is that the naphtha solvent is encapsulated along with the insecticide, reducing the proportion of insecticide and creating other problems in handling, packaging, storage and use of the product.

According to the invention, we provide substantially solvent-free microcapsules comprising from at least 10 to 75% by weight of the microcapsules of an insecticide selected from methomyl, oxamyl and mixtures of methomyl with an insecticide selected from oxamyl, aldicarb, diflubenzuron, chlordimeform, methyl parathion, ethylparathion, EPN, fenvalerate, permethrin, decamethrin, cypermethrin, carbaryl, and leptophos, and an outer encapsulating wall of cross-linked polyurea.

The microcapsules can be prepared by (a) dissolving methomyl, oxamyl or mixtures of methomyl with other insecticides from the above list in methylene chloride containing a polyisocyanate or a mixture of polyisocyanate with diisocyanate, (b) emulsifying the solution into a cooled aqueous surfactant solution, (c) adding a diamine or polyamine or a mixture of the two to form a cross-linked polyurea encapsulating shell around droplets of the emulsified solution and (d) removing the methylene chloride.

Methylene chloride, which is used as the solvent in preparing the microcapsules of this invention, has a higher volatility than the active ingredients and will unexpectedly pass through the polyurea encapsulating wall with no damage to the wall. Thus, the insecticide microcapsules of this invention are substantially solvent-free. The terms "substantially solvent-free" and "solvent free" as used herein mean that the microcapsules contain not more than 1% by weight of solvent.

A solvent-free product has distinct advantages over the naphtha solution encapsulated products known in the art. The solvent-free microcapsules contain a higher concentration of active ingredient, and they are easier and safer to package and handle. Hence, there is less danger of toxicity to humans, and the product is easier to apply to crops.

#### DETAILED DESCRIPTION OF THE INVENTION

The microcapsules of this invention may be prepared by the following process:

A. A methylene chloride solution A is prepared containing:

- (1) 10-50 weight percent of active ingredient, methomyl, oxamyl or a mixture of methomyl and an insecticide selected from oxamyl, aldicarb, diflubenzuron, chlordimeform, methyl parathion, ethylparathion, EPN, fenvalerate, permethrin, decamethrin, cypermethrin, carbaryl, and leptophos. Methomyl and oxamyl are preferred as active ingredients. Any desired ratio of active ingredients may be used if mixtures thereof are to be encapsulated.

- (2) 0-30 Weight percent of the final microcapsule weight of a methylene chloride soluble inert polymer, e.g., polymethylmethacrylate, polystyrene, styrene copolymer or methylmethacrylate copolymers, etc.
- (3) A polyisocyanate or a mixture of a polyisocyanate with a diisocyanate. Preferred is a mixture of an aromatic diisocyanate with a polyisocyanate, and the preferred diisocyanate is 2,4-toluene diisocyanate.

The term polyisocyanate as used herein means an organic compound having at least three functional isocyanate groups. Preferred for use in this invention are aromatic polyisocyanates such as

polymethylene polyphenylisocyanate, also written as polymethylene phenyl isocyanate-PAPI® (Upjohn Co.); triphenylmethane-4,4',4"-triisocyanate.

Examples of suitable diisocyanates are:

2,4-toluene diisocyanate  
2,6-toluene diisocyanate  
mixtures of 2,4- and 2,6-toluene diisocyanates  
hexamethylene diisocyanate  
para-phenylene diisocyanate  
meta-phenylene diisocyanate  
naphthalene-1,5-diisocyanate  
tetrachloro-m-phenylene diisocyanate  
dichlorodiphenyl methane diisocyanate  
4,4-diphenyl diisocyanate  
bitolylene diisocyanate  
diphenylether diisocyanates  
dimethyl diphenyl diisocyanates.

When a diisocyanate is used, the quantity of polyisocyanate will most desirably be at least 10 mole percent based on diisocyanate. Preferred is 10 to 25 mole percent of polyisocyanate based on diisocyanate.

5 The total quantity of isocyanate (diisocyanate plus polyisocyanate) should be such that the concentration of insecticide in the final microcapsules is about 10 to 75% by weight, preferably 20-55% by weight.

10 B. The solution A is added to a cooled (0-15°C) aqueous solution B of a suitable surfactant or mixture of surfactants, such as polyvinyl alcohols. The surfactant emulsifies A into B and maintains the dispersion while polymerization (Step C) occurs to  
15 form the walls of the microcapsule. The amount of surfactant needed can be determined by those skilled in the art, but the surfactant must be present in sufficient quantities to form the desired emulsion. The volume ratio of A to B is such that A is 30-50  
20 volume percent of A + B. The upper limit of the volume percent range of A is determined by the need to maintain an oil-in-water emulsion, avoiding an emulsion inversion. The mixture of A and B is agitated in order to form an emulsion containing the desired  
25 particle size (5-150 $\mu$ ) of droplets; preferably 10-50 $\mu$ . Larger droplets of 150-750  $\mu$  particle size can also be prepared depending on the end use of the microcapsule formulation.

30 C. To the A + B emulsion at 0-15°C is added a diamine (0-100 weight percent of total amine) such as ethylenediamine, or a polyamine (0-100 weight percent of total amine) such as diethylenetriamine, or a mixture of di- and polyamine.  
35

The term polyamine as used herein means an aliphatic amine having at least three primary or secondary amine groups, such as

5 diethylenetriamine  
triethylenetetramine  
tetraethylenepentamine  
pentaethylenehexamine.

The term diamine means an aliphatic amine having two primary or secondary amine groups, such as  
10 ethylenediamine  
hexamethylenediamine  
piperazine  
tetramethylenediamine.

15 Either a polyamine or a diamine can be used, but is preferred that the amine component be 50-100 mole percent diamine and 0-50 mole percent polyamine. In the most preferred embodiment of this invention, the amine component should be 75-85 mole percent diamine and 15-25 mole percent polyamine. During  
20 polymerization, the temperature is maintained at 10-35°C. The amine can be added as such, but it is preferably added as an aqueous solution containing at least 20 weight percent amine. The ratio of amines to isocyanate is 95-300-mole percent, preferably 110-  
25 200 mole percent. After polymerization is complete, the excess amine can be neutralized to a range of pH 5-8 with acid such as hydrochloric or phosphoric acid to avoid base decomposition of any methomyl or oxamyl present in the aqueous phase.

30 D. The polymerization step yields the desired insecticide microcapsules which also contain methylene chloride. At this point, the polyurea polymer encapsulating wall is swollen and tacky, and the particles,  
35 i.e., microcapsules, tend to adhere to one another

which makes isolation thereof very difficult. Therefore, the methylene chloride must be removed from the microcapsules, and this may be accomplished by passing an air or nitrogen stream over the surface of the slurry from step C or by applying a vacuum thereto. Quite unexpectedly, the methylene chloride will pass through the microcapsule wall without damaging the polyurea. The insecticidal core remains intact within the encapsulating wall.

5 E. The microcapsules, usually about 5-150  $\mu$  in size, can be isolated by conventional techniques, e.g., concentration or filtration and then washed with water.

In some instances, it may be desirable to eliminate the isolation step and use the product as is or diluted with water or additional materials, such as thickeners to improve formulation characteristics.

Methomyl has a high degree of contact activity when applied topically to insects. Some of this activity may be lost if the methomyl is encapsulated and not available to contact the outer surface of an insect. Therefore, it may be desirable to mix some unencapsulated methomyl with the microencapsulated methomyl formulation to impart the contact insecticidal activity. Also, to impart other desired insecticidal effects, it may be desirable to mix methomyl microcapsules with other insecticides such as diflubenzuron, chlordimeform, fenvalerate, permethrin, decamethrin, cypermethrin or methyl parathion microcapsules (prepared as taught in U.S. Patent Specification No. 3,959,464). Such compositions comprise a further feature of the invention.

The following examples are illustrative of the instant invention. Unless otherwise indicated, all parts are by weight and all temperatures in  $^{\circ}\text{C}$ .

In all examples, the surfactant used was a poly-vinylalcohol, Elvanol® 50-42 (E. I. du Pont de Nemours & Co.), which was prepared as a 0.5% aqueous solution



by dissolving in water using an Osterizer blender.

As used herein, the terms "cross-linked polyurea" and "cross-linked polyurea polymer" mean a polymer of repeating ureido groups with linkages between adjacent polymer chains formed by the reaction of amine and isocyanate functionality not used in linear chain growth. Cross-linking in condensation polymerization is generally achieved by using polymerizable compounds containing more than two functional groups, e.g., triamines and triisocyanates in the case of cross-linked polyureas.

#### Example 1

The following solutions were prepared:

- A. Organic phase which was prepared just prior to use.
- |    |        |  |
|----|--------|--|
| 15 | 15 ml  | methylene chloride                       |
|    | 15 g   | methomyl                                 |
|    | 2.6 ml | 2,4-toluene diisocyanate                 |
|    | 0.7 g  | PAPI® polymethylene polyphenylisocyanate |
- B. Aqueous phase
- |    |       |  |
|----|-------|--|
| 20 | 60 ml | 0.5% aqueous Elvanol® 50-42 polyvinyl alcohol solution |
|----|-------|--|
- C. Amine solution of
- |    |        |                     |
|----|--------|---------------------|
| 25 | 20 ml  | water               |
|    | 3.6 ml | ethylenediamine     |
|    | 1.4 ml | diethylenetriamine. |

To a 250 ml Erlenmeyer flask equipped with a magnetic stirrer, was added 60 ml of 0.5% polyvinyl alcohol solution B. After cooling solution B in an ice bath to about 5°C, the organic phase, solution A, was added with vigorous stirring. This mixture was stirred for 30 seconds to form a stable emulsion, whereupon the previously chilled amine solution C was added (with temperature control <15°C) and the stirring rate slowed.

The resulting slurry of microcapsules was allowed to warm to room temperature and was stirred at ambient temperature overnight with an air stream passing over the surface to remove methylene chloride.

- 5 The microcapsules were isolated by first centrifuging to remove supernatant liquid, washing with water and filtering. The resulting tan powder was allowed to dry on the funnel. The isolated powder, 10.0 g, was screened through a 60 mesh sieve.
- 10 Elemental sulfur analysis indicated a methomyl concentration of 53.5%, with the balance cross-linked polyurea polymer. Less than 0.2% methylene chloride as determined by elemental chlorine analysis was present. The particle size of the microcapsules was 30-70  $\mu$ ,  
 15 as determined by microscopic investigation.

#### Example 2

- In this example an inert polymer, poly(methyl methacrylate), Elvacite® 2010 (E. I. du Pont de Nemours & Co.), was added to the organic phase. The following solutions were prepared:

##### A. Organic phase

- |                  |        |                             |
|------------------|--------|-----------------------------|
|                  | 20 ml  | methylene chloride          |
|                  | 4.2 g  | Elvacite® 2010              |
| 25               | 17 g   | methomyl                    |
|                  | 2.6 ml | 2,4-toluene diisocyanate    |
|                  | 1.8 g  | PAPI®                       |
| B. Aqueous phase |        |                             |
|                  | 50 ml  | 0.5% aqueous Elvanol® 50-42 |

##### 30 C. Amine solution of

- |  |        |                     |
|--|--------|---------------------|
|  | 10 ml  | water               |
|  | 3.6 ml | ethylenediamine     |
|  | 1.4 ml | diethylenetriamine. |

- 35 The same procedure as in Example 1 was followed. 17.2 g of microcapsules were isolated

10

which were analyzed by elemental sulfur analysis to be 48% methomyl and which contained less than 0.2 % methylene chloride as determined by elemental chloride analysis. The particle size was 30-70  $\mu$  as determined by microscopic investigation.

Example 3

In this example, polystyrene (Shell 314) was used as added inert polymer to the organic phase. The following solutions were prepared:

- 10 A. Organic phase
- |        |                          |
|--------|--------------------------|
| 20 ml  | methylene chloride       |
| 4.2 g  | polystyrene (Shell 314)  |
| 17 g   | methomyl                 |
| 2.6 ml | 2,4-toluene diisocyanate |
| 1.0 g  | PAPI®                    |
- 15 B. Aqueous phase
- |       |                             |
|-------|-----------------------------|
| 60 ml | 0.5% aqueous Elvanol® 50-42 |
|-------|-----------------------------|
- C. Amine solution of
- |        |                    |
|--------|--------------------|
| 10 ml  | water              |
| 3.6 ml | ethylenediamine    |
| 1.4 ml | diethylenetriamine |
- 20

The same procedure as in Example 1 was followed to give 16.0 g of isolated microcapsules which analyzed by sulfur analysis to be 27.8% methomyl and contained <0.2 % methylene chloride as determined by elemental chlorine analysis. The particle size was 30-70  $\mu$  as determined by microscopic investigation.

25

Example 4

The following solutions were prepared:

- 30 A. Organic Phase
- |         |                          |
|---------|--------------------------|
| 90 ml   | methylene chloride       |
| 90 g    | methomyl                 |
| 46.2 ml | 2,4-toluene diisocyanate |
| 21.6 g  | PAPI®                    |
- 35

## B. Aqueous phase

220 ml

0.5% aqueous Elvanol® 50-42

## C. Amine solution of

50 ml

water

5

40.8 ml

ethylenediamine

16.6 ml

diethylenetriamine.

To a 500 ml baffled resin kettle was added 290 ml of solution B. After cooling to 15°C in an ice bath, the organic phase, solution A, was added with vigorous stirring. After stirring for 2 minutes, the stirring rate was slowed and previously chilled solution C was added. The temperature of the mixture quickly rose to 32°C and slowly cooled over a 30-minute period. The ice bath was removed and an air stream passed over the surface of the slurry for 6 hours to remove methylene chloride.

The microcapsules were isolated by centrifuging to remove supernatant liquid, redispersing in 150 ml of water, filtering and air drying to give 149.0 g of a tan powder containing 41.9% methomyl with a particle size range of 10-40  $\mu$  with an average size of 21  $\mu$ , as determined by Coulter Counter.

Example 5

In this example, an 80/20 mixture by weight of 2,4- and 2,6-toluene diisocyanate, Hylene® (E. I. du Pont de Nemours & Co.) was used as the diisocyanate. The following solutions were prepared.

## A. Organic phase

30

15 ml

methylene chloride

15 g

methomyl

5.2 ml

80/20 mixture of 2,4- and 2,6-toluene diisocyanate

1.4 g

PAPI®

35

12

## B. Aqueous phase

50 ml

0.5% aqueous Elvanol® 50-42

## C. Amine solution of

10 ml

water

5

7.2 ml

ethylenediamine

2.8 ml

diethylenetriamine.

To a 500 ml baffled resin kettle was added 50 ml of solution B. After cooling to 10°C in an ice bath, the organic phase, solution A, was added with vigorous stirring. After stirring for 45 seconds the stirring rate was slowed and previously chilled solution C was added. After stirring the resulting slurry for 30 minutes, an air stream was passed over the surface for 2 hours to remove methylene chloride.

The microcapsules were isolated as in the previous examples to give 13.2 g of a tan powder which analyzed as 44.9% methomyl by liquid chromatography. The average particle size was 18-20  $\mu$  as determined by microscopic investigation.

Formulation

Useful formulations of the microcapsules described in the previous examples can be prepared as wettable powders or aqueous suspensions in conventional ways. These sprayable formulations can be extended in suitable media and used at spray volumes of from a few pints to several hundred gallons per acre. High strength compositions are used primarily as intermediates for further formulation. The formulations, broadly, contain about 10% to 99% by weight of microcapsules and at least one of (a) about 1% to 20% surfactant(s) and (b) about 9% to 99% solid or liquid inert diluent(s). More specifically, they will contain these ingredients in the following approximate proportions:

35

13

Percent by Weight\*

	<u>Microcapsule</u>	<u>Diluent(s)</u>	<u>Surfactant(s)</u>
Wettable Powder	19-99	0-80	1-10
Aqueous Suspensions	10-60	30-89	1-20

5

\* Weight of microcapsule plus at least one of a Surfactant or Diluent equals 100 weight percent.

Higher ratios of surfactant to active ingredient are sometimes desirable, and are achieved by incorporation into the formulation or by tank mixing.

Typical solid diluents are described in Watkins et al., "Handbook of Insecticide Dust Diluents and Carriers", 2nd Edn., Dorland Books, Caldwell, N. J. The more finely divided diluents are preferred for the wettable powders of this invention. Water is the preferred liquid diluent, but may contain other water-soluble materials such as alcohols, glycols or ketones to provide improved freeze resistance, for example, methanol, ethanol, propylene glycol, acetone, or the like. "McCutcheon's Detergents and Emulsifiers Annual", McCutcheon Division, MC Publishing Co., Ridgewood, New Jersey, as well as Sisely and Wood, "Encyclopedia of Surface Active Agents", Chemical Publ. Co., Inc., New York, 1964, list surfactants and recommended uses.

All formulations can contain minor amounts of additives to reduce foam, caking, corrosion, microbiological growth, etc., or to buffer the pH.

The methods of making such compositions are well known. Fine solid compositions are made by blending.

Aqueous suspensions may be obtained directly from the encapsulation slurry without isolation of the dried microcapsules by warming and/or passing air or nitrogen through the slurry to remove methylene chloride. Any additionally desired diluents or surfactants may then be added.

Those skilled in the art of formulations will recognize that the above formulations are only examples of representative formulations and other product forms are possible.

5 In the following examples, ingredient proportions are by weight.

Example 6

Wettable Powder

	Methomyl microcapsule	40%
10	Dioctyl sodium sulfosuccinate	1.5%
	Sodium lignin sulfonate	3%
	Low viscosity methyl cellulose	1.5%
	Attapulgate	54%

15 The ingredients are thoroughly blended and sifted through a U.S.S. No. 50 sieve (0.3 mm opening) before packaging. If desired all ingredients except the microcapsules may be ground in a hammer or fluid energy mill to reduce the particle size of these components. The microcapsules can then be blended into this ground  
20 premix.

Example 7

Wettable Powder

	Methomyl microcapsule	96%
25	Sodium alkyl naphthalene sulfonate	2%
	Sodium lignin sulfonate	2%

The ingredients are thoroughly blended and sifted through a U.S.S. No. 50 sieve (0.3 mm opening) before packaging.

30

35

Use

The microcapsules of this invention are useful in agriculture for control of insects and nematodes which are controlled by methomyl, oxamyl and mixtures of methomyl with other insecticides listed previously. As demonstrated in the following examples, improved residual insecticidal and nematocidal properties as well as decreased phytotoxicity are obtained with controlled release methomyl microcapsules.

The insects are controlled by applying microcapsules to the locus of infestation, to the area to be protected, or to the pests themselves. For the control of insects on agricultural crops, the microcapsules are generally applied to the foliage or other plant parts which are infested or which are to be protected. Effective amounts to be applied depend upon the specific compound used, the species to be controlled, its life stage, its size and location, the amount of rainfall, the time of year, moisture, temperature, type of application, plant spacing, and other variables. In general, .05 to 10 Kg of active ingredient per ha may be required for insect control in agriculture with rates of 0.15 to 5 Kg/ha usually being sufficient. In large scale field operations, rates in the range of 0.25 to 3 Kg/ha are generally used.

Nematodes are controlled by applying the microcapsules to the locus of infestation, to the area to be protected or to the pest themselves. For the control of nematodes in agricultural crops, a microcapsule formulation of this invention is generally applied to a portion of the plant or surrounding soil which is infested or which is to be protected. Effective amounts to be applied depend upon the species to be controlled, its life stage, its size and location, the amount of



rainfall, the time of year, moisture, temperature, soil type, percentage of area treated, type of application, and other variables. In general, 3 to 30 Kg of active ingredient per ha may be required for nematode control in agriculture with rates of 5 to 10 Kg/ha usually being sufficient in many situations.

The methomyl microcapsules possess significant advantages over prior art compounds. For example, their improved residual insecticidal and nematocidal activity can reduce the need for closely spaced multiple applications resulting in greater economy to the grower and dissemination of less pesticide in the environment. There is also less chance that the pesticide applied in this manner will be damaging to plants. A specific advantage of this type is the reduced side-effect on cotton. Treated leaves remain green and free of reddening that may result when the same pesticides are applied in other forms.

The microcapsules of this invention can be mixed with fungicides, bactericides, acaricides, as well as other nematocides, insecticides, or other biologically active compounds in order to achieve desired results with a minimum expenditure of time, effort and material. Amounts of these biologically active materials added for each part by weight of the composition of this invention may vary from 0.05 to 25 parts by weight.

The microcapsules of this invention can also be mixed with unencapsulated methomyl, oxamyl or other insecticide or nematocide, to obtain enhanced effect, immediately upon application, with the improved residual insecticidal or nematocidal activity which derives from the encapsulation. Such mixtures may be in the form of combined single-package products, or they may be accomplished in the spray tank, by tank-mixing. The ratio of unencapsulated to encapsulated active ingredient can vary widely but would usually be from 1:10 to 10:10.

Example 8

The foliage of red kidney bean plants in the two-leaf stage was sprayed to run-off with dispersions of microcapsules of this invention at various concentrations. Dispersions were prepared by diluting appropriately weighed quantities of the microcapsules to 100 ml with water containing surface active agent, sodium lauryl sulfate (DuponoleC) (E. I. du Pont de Nemours & Co.) at 1:5000. After drying, the plants were placed under artificial light in a room maintained at  $25 \pm 2^\circ\text{C}$ ,  $54 \pm 5\%$  RH. Two days thereafter, leaves were excised from the plants and placed in covered 10 cm petri dishes along with moist filter paper to keep them fresh. Ten southern armyworm larvae were placed in each dish. Tests were run in duplicate. The units were kept in a room maintained at  $25 \pm 2^\circ\text{C}$ ,  $54 \pm 5\%$  RH. Mortality results were recorded two days thereafter. Seven days after the plants had been dried and placed in the relative humidity room, additional leaves were excised from the plants and tested in the same manner as those excised after two days.

	<u>Microcapsule Formulation</u>	<u>Active Ingredient* Concentration in Spray %</u>	<u>% Larvae Dead</u>	
			<u>2 days</u>	<u>7 days</u>
25	Example 1	0.01	100	100
		0.005	85	95
	Example 2	0.01	100	100
		0.005	90	95
	Example 3	0.01	100	-
		0.005	95	-
30	Example 4	0.01	100	100
		0.005	100	100
	Example 5	0.01	100	100
		0.005	100	100
	Untreated Control	-	0	0
	Uncapsulated methomyl	0.01	5	0
35				

\* Active ingredient refers to the methomyl concentration in the spray.

Example 9

Potted cotton plants approximately 30 cm high having 5-6 true leaves were sprayed to run-off with aqueous dispersions of the following microcapsule formulations of this invention at 500 ppm. The sprays contained surface active agent (Duponol® C) at a concentration of 1:500. Other sets of plants were similarly treated with methomyl. After drying, plants were set out in the greenhouse and held for observation.

<u>Microcapsule Formulation</u> (500 ppm AI) <sup>1</sup>		<u>Rating<sup>2</sup> (8 days)</u>
<u>Test A</u>		
	Example 1	0
15	Example 3	3R
	Unencapsulated Methomyl	5R
	Untreated Control	0
<u>Test B</u>		
	Example 2	0.2R
20	Unencapsulated Methomyl	4R
	Untreated Control	0
<u>Test C</u>		
	Example 4	0
25	Unencapsulated Methomyl	3R
	Untreated Control	0
<u>Test D</u>		
	Example 5	0.25R
	Unencapsulated Methomyl	4R
30	Untreated Control	0
<sup>1</sup> AI - active ingredient (methomyl)		
<sup>2</sup> "R" denotes typical methomyl effect, i.e., reddening of older leaves, slight puckering and black stippling of younger leaves. Rating is on the basis of 0 to 10, with 10 indicating total leaf area involvement.		

Claims:

1. Substantially solvent-free microcapsules comprising from at least 10 to 75% by weight of the microcapsules of an insecticide selected from methomyl, oxamyl and mixtures of methomyl and an insecticide selected from oxamyl, aldicarb, diflubenzuron, chlordimeform, methyl parathion, ethylparathion, EPN, fenvalerate, permethrin, decamethrin, cypermethrin, carbaryl and leptophos within an encapsulating wall of cross-linked polyurea.
2. Microcapsules as claimed in claim 1 which contains 20-55% by weight insecticide.
3. Microcapsules as claimed in claim 1 or claim 2 wherein the microcapsules are 5-150  $\mu$  in average particle size.
4. Microcapsules as claimed in any of claims 1 to 3 in which the insecticide is methomyl or oxamyl.
5. Microcapsules as claimed in any of claims 1 to 4 in which the core contains a methylene chloride soluble inert polymer in an amount up to about 30% by weight of the total microcapsule weight.
6. Microcapsules as claimed in claim 5 in which the inert polymer is selected from polymethylmethacrylate and polystyrene.
7. An insecticidal composition which comprises microcapsules of any of claims 1 to 6 in admixture with an unencapsulated insecticide in a ratio of from 1:10 to 1:1.
8. A composition as claimed in claim 7 wherein the unencapsulated insecticide is methomyl.
9. A composition as claimed in any of the preceding claims comprising from 10-99% by weight of microcapsules as defined in claim 1 and at least one of (a) from 1% to 20% surfactant(s) and (b) from 9 to 99% of solid or liquid inert diluent(s), all percentages being by weight.

10. A process for preparing microcapsules as claimed in claim 1 including the steps of (a) dissolving methomyl, oxamyl, or a mixture of methomyl and an insecticide selected from the group oxamyl, aldicarb, diflubenzuron, chlordaneform, methyl parathion, ethyl-parathion, EPN, fenvalerate, permethrin, decamethrin, cypermethrin, carbaryl and leptophos in methylene chloride containing polyisocyanate or a mixture of a polyisocyanate and diisocyanate, (b) emulsifying the solution into a cooled aqueous surfactant solution, (c) adding a diamine or polyamine or a mixture of the two to form a cross-linked polyurea encapsulated shell around droplets of the emulsified solution, and (d) removing the methylene chloride.

11. A process as claimed in claim 10 wherein the methylene chloride solution in step (a) contains diisocyanate in addition to polyisocyanate and a mixture of diamine and polyamine is added to the emulsion in step (c).

12. A process as claimed in claim 10 or claim 11 wherein the concentration of polyisocyanate is about 10 to 25 mole percent based on diisocyanate and the concentration of polyamine is about 15-25% mole percent based on total amine.

13. A process as claimed in any of claims 10-12 wherein both the diisocyanate and polyisocyanate are aromatic isocyanates.

14. A process as claimed in any of claims 10-13 wherein the diisocyanate is 2,4-toluene diisocyanate and the polyisocyanate is polymethylenepolyphenyl isocyanate.

15. A process as claimed in any of claims 10-14 wherein the diamine is ethylenediamine and the polyamine is diethylene triamine.

16. A process as claimed in any of claims 10-15 wherein the reaction temperature is 0-35°C.

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17. A method of controlling an insect pest by applying to the locus of said pest an effective amount of an insecticidal composition characterised in that said insecticidal composition is a composition of any of claims 1 to 9.

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54 Insecticidal compositions, and preparation and use thereof.

57 Insecticidal compositions and the preparation and use thereof are disclosed. Substantially solvent-free microcapsules comprising a core of an insecticide selected from the group consisting of methomyl, oxamyl, and mixtures of methomyl with oxamyl or other known insecticides within an encapsulating wall of a cross-linked polyurea are disclosed. The microcapsules may be made by dissolving the insecticide(s) in methylene chloride containing a polyisocyanate, emulsifying the solution and adding a diamine or polyamine to form a cross-linked polyurea encapsulating shell around droplets of the emulsifying solution, followed by removal of methylene chloride. Compositions containing the microcapsules are also disclosed.

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European Patent  
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# EUROPEAN SEARCH REPORT

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Application number  
EP 79 30 1568

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. 7)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
D	<u>GB - A - 1 371 179 (STAUFFER)</u> * Claims; page 2, lines 92-97; page 4, lines 94-113; page 9, lines 38-75 *	1-17	A 01 N 25/28 A 01 N 47/24
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	<u>US - A - 3 577 515 (J.E. VANDEGAER)</u> * Column 7, lines 4-6 and 41- 47; column 10, lines 27-33; example 17 *	1-17	
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	<u>FR - A - 2 090 862 (FUJI PHOTO FILM)</u> * Page 1, lines 6-26 and page 8, lines 21-25 *	1	TECHNICAL FIELDS SEARCHED (Int. Cl. 7)
	--		A 01 N 25/28 A 01 N 47/24
	<u>DE - A - 2 017 808 (ERZ- UND KOHLE FLOTATION)</u> * Claim 1; page 6, lines 10-13 *	7,8	
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			CATEGORY OF CITED DOCUMENTS
			X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons
			&: member of the same patent family, corresponding document
The present search report has been drawn up for all claims			
Place of search The Hague	Date of completion of the search 28-11-1979	Examiner DECORTE	

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